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$FeCl_3$/ AgOTf Catalyzed Hydroarylation Reactions of Aryl-substituted Alkynes with Different Electron-rich Arenes

Md. Ataur Rahman[1]* and Tsugio Kitamura[2]
[1]Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh.
[2]Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, Honjo-machi, Saga, 840-8502, Japan.
*Corresponding author (e-mail: ataur_ju@yahoo.com)

There are many synthetic methods for the direct formation of carbon-carbon bond between arenes and alkynes. Metal-catalyzed hydroarylation reaction is one of the synthetic methods for the direct formation of new carbon-carbon bond between arenes and alkynes. The hydroarylation reaction of aryl-substituted alkynes with arenes proceeded smoothly in the presence of $FeCl_3$/AgOTf catalyst system in a mixed solvent of trifluoroacetic acid and dichloromethane at 30ºC and yielded aryl-substituted alkenes in moderate to high yields. Electron rich arenes gave high yields whereas the relatively less electron rich arenes gave norminal yields.

Key words: $FeCl_3$/AgOTf catalyst; hydroarylation; alkynes; arenes; arylalkenes

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Catalytic and direct functionalization of simple arenes through the formation of new carbon-carbon bond is important for the synthesis of various valuable organic compounds in one step [1–7]. The process gives a very simple, clean and economical method for the synthesis of various substituted aromatic compounds directly in one step from simple arenes, because in this process aromatic C-H bond directly acts as a functional group and it does not require the pre-functionalization like halogenation of aromatic C-H bond. This direct carbon-carbon bond formation method not only reduces the reaction steps but also avoids the use of toxic halogenated compounds. In general, Friedel-Crafts reaction of aromatic compound is one of the fundamental reactions for the direct formation of the new carbon-carbon bond, but these reactions require more than equimolar amount of a Lewis acid such as aluminium (III) chloride [8–9].

As a result, for over a century organic chemists have sought to develop new, clean and efficient direct carbon-carbon bond forming methods [10]. To date, different methods have been developed for the direct formation of new carbon-carbon bond between arenes and olefins [11–24]. All of these improved methods were catalyzed by transition metals or Lewis acid-metals. Of these differently developed methods, hydroarylation reaction is well-known method for the direct formation of new carbon-carbon bond between arenes and olefins.

No doubt the reported metal-catalyzed hydroarylation reactions are excellent, efficient and powerful synthetic methods for the direct formation of new carbon-carbon bond between arenes and olefins. But still, there are some limitations, that transition metal-catalyzed hydroarylation reactions require high temperature, strong acidic conditions and special cautions for handling metal catalysts under an inert atmosphere. Furthermore, contamination of pharmaceutical materials with a trace amount of toxic metals in the processes of manufacture causes a serious problem. Besides these, literature survey reveals that in most cases the reported transition metals alone can not act as an efficient catalyst. An appropriate activating agent is required to improve the catalytic activity of the transition metals. In many cases, more than one activating agents and more than equimolar amounts of activating agents are required to improve the catalytic activity of the reported transition metals.

Thus a lot of hazardous salty waste products formed during the reactions that may be the cause of the pollution of the environment. Some transition metals and some catalyst activating agents are very expensive that not only increase the reagent cost but also increase the production cost. Therefore, if the expensive, rare and toxic metals could be replaced by inexpensive, non-toxic, readily available and environmentally-friendly metals, the direct carbon-carbon bond formation reaction between arenes and olefins would be more valuable for the synthesis of substituted aromatic compounds. Iron is a cheap, readily available, non-toxic and environmentally-friendly transition metal which shows increasing and promising catalytic ability in many organic syntheses [25–29].

Lu *et al.* reported the hydroarylation reaction of aryl-substituted alkynes with simple and substituted arenes in the presence of $FeCl_3$ in CH_3NO_2 solvent without using any additives under mild conditions [30]. Aryl-substituted alkynes undergo hydroarylation reaction with electron rich arenes smoothly to afford 1, 1-diarylalkenes.

To improve the catalytic activity of $FeCl_3$ it is necessary to increase the cationic property of $FeCl_3$ because the hydroarylation reaction of olefins is considered to proceed through the electrophilic aromatic substitution. Silver triflate, AgOTf, is thought to undergo ligand-exchange reaction with $FeCl_3$ and forms more cationic and more active $Fe(OTf)_3$ species [31]. Very recently it has been reported that the hydroarylation reaction of electron-deficient propiolic acid with different electron rich arenes proceeds smoothly in the presence of $FeCl_3$/AgOTf in TFA solvent [32–33].

Therefore, by extending the reported hydroarylation method of propiolic acid with different electron rich arenes, an attempt has been made to carry out the hydroarylation reaction of aryl-substituted alkynes with different electron rich arenes using $FeCl_3$/AgOTf in TFA and dichloromethane (DCM) solvent.

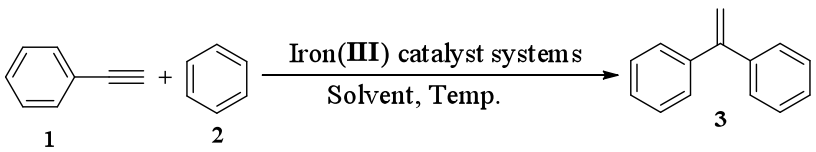
Present hydroarylation method is much simpler and milder than those of the reported methods. We have studied the hydroarylation reaction of alkynes with different arenes using $FeCl_3$/AgOTf in TFA and DCM solvent to apply it to different aryl-substituted alkynes with different electron rich arenes.

RESULTS AND DISCUSSION

Direct preparation of 1,1-diarylalkenes was carried out from the corresponding arenes and alkynes using $FeCl_3$ /AgOTf catalyst in a mixed solvent system of TFA and CH_2Cl_2 at 30ºC. In the present study, to have an effective catalyst system and to optimize the reaction conditions initially, the work was concentrated on the efficiency of the hydroarylation reaction of phenylacetylene 1 with benzene 2 in the presence of a different catalyst and solvent systems under different reaction conditions (Scheme 1). The results are given in Table 1.

Optimization of the Reaction Conditions

The reaction using $FeCl_3$/AgOTf catalyst system in the presence of TFA at 30ºC for 60h afforded the hydroarylation product 3 in 18% (Entry 3). Increasing the amount of $FeCl_3$ and AgOTf did not improve the yield (Entry 4). No hydroarylation reaction occurred in the presence of the catalyst systems $FeCl_3$/TFA and only in the presence of $FeCl_3$ (Entries 1 and 6). Furthermore, elevation of



Scheme 1. Hydroarylation reaction of phenylacetylene 1 with benzene 2 in the presence of different catalyst and solvent systems.

Table 1. Hydroarylation reaction of phenylacetylene 1 with benzene 2 in the presence of different catalyst and solvent systems[a].

Entry	Catalyst	Temp(ºC)	Time(h)	Product	Yield(%)[b]
1	$FeCl_3$/TFA	30	72	No product	-c
2	$FeCl_3$/AgOTf	30	72	3	10d
3	$FeCl_3$/AgOTf/TFA	30	60	3	18e
4	$FeCl_3$/AgOTf/TFA	30	60	3	14f
5	$FeCl_3$/AgOTf/TFA	45	60	3	17g
6	$FeCl_3$	30	60	No product	-h
7	$FeCl_3$/AgOTf	30	60	No product	-i

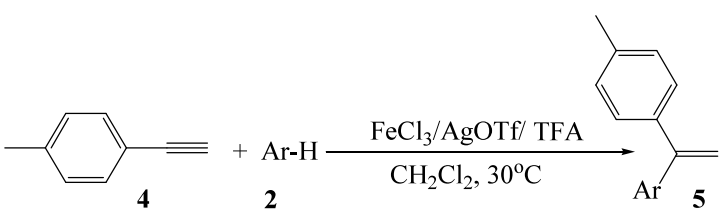
[a]Reaction conditions : Benzene 2 (100.0 mmol), phenylacetylene 1(1.0 mmol), CH_2Cl_2 (1.0 ml), molecular sieve 4A(3–4 pieces, 0.20~0.25g).
[b]Isolated yield based on phenylacetylene 1.
[c]$FeCl_3$ (0.10 mmol), TFA (1.0 ml).
[d]$FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol).
[e]$FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 ml).
[f]$FeCl_3$ (0.20 mmol), AgOTf (0.60 mmol), TFA (1.0 ml).
[g]$FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 ml), $(CH_2)_2Cl_2$ (1.0 ml).
[h]$FeCl_3$ (0.10 mmol), CH_2Cl_2 (1.0 ml).
[i]$FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol), CH_3NO_2 (1.0 ml).

the reaction temperature did not improve the yield (Entry 5). When the reaction was carried out using $FeCl_3$/AgOTf catalyst system in the absence of TFA afforded the hydroarylation product 3 in 10% yield in CH_2Cl_2 solvent only (Entry 2), but the reaction in nitromethane solvent did not form any hydroarylation products (Entry 7). From the above screening results, it was found that the Entry 3 is the optimum condition for the reaction.

Scope of the Hydroarylation Reaction

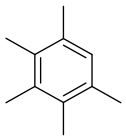
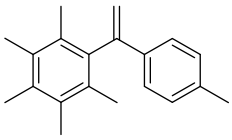
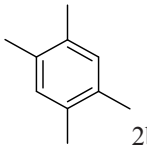
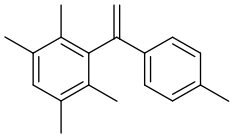
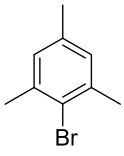
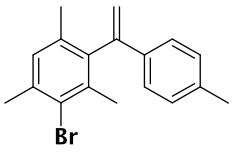
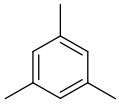
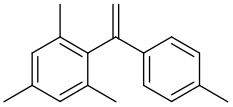
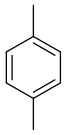
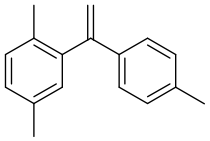
Using the reaction conditions of Entry 3 in Table 1 the hydroaylation reaction of 4-methylphenylacetylene 4 was conducted with different electron rich arenes 2 (Scheme 2). The results are given in Table 2. In the reaction of 4-methylphenylacetylene 4 with electron rich arenes 2a-2d, excellent yields of the hydroarylation products 5 were obtained (Entries 1-4). However, the moderately electron rich arene *p*-xylene 2e showed less reactivity with 4-methylphenylacetylene 4 and the yield of the hydroarylation product 5e was 9 % (Entry 5).

Next, the reaction of 4-fluorophenylacetylene 6 was examined with various electron rich arenes 2 under the above reaction conditions (Scheme 3). The results of the reactions are shown in Table 3.

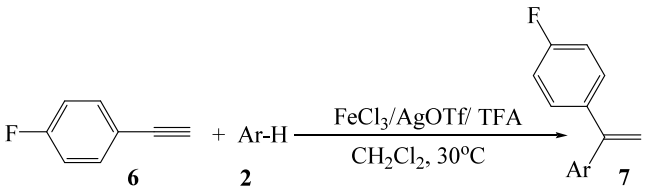


Scheme 2. Hydroarylation reaction of 4-methylphenylacetylene 4 with different arenes 2 in the presence of $FeCl_3$/ AgOTf catalyst system.

Table 2. Hydroarylation reaction of 4-methylphenylacetylene 4 with different electron rich arenes 2 in the presence of $FeCl_3$/AgOTf catalyst system[a].

Entry	Arene 2	Time(h)	Product 5	Yield (%)[b]
1	 2a	30	 5a	78
2	 2b	24	 5b	84
3	 Br 2c	60	 Br 5c	63
4	 2 d	24	 5d	81
5	 2 e	24	 5e	9

[a]Reaction conditions: Arene 2 (5.0 mmol), alkyne 4 (1.0 mmol), $FeCl_3$ (.0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 ml), CH_2Cl_2 (3.0 ml), molecular sieve 4A(3–4 pieces, 0.20~0.25g) at 30ºC.
[b]Isolated yield based on 4-methylphenylacetylene 4.



Scheme 3. Hydroarylation reaction of 4-fluorophenylacetylene 6 with different arenes 2 in the presence of $FeCl_3$/ AgOTf catalyst system.

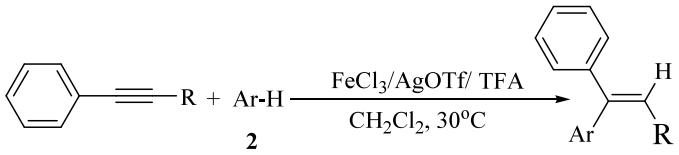
The reaction of electron rich arenes 2a-2d gave the hydroarylation products 7 in good yields (Entries 1-4). The moderately electron rich arenes such as *p*-xylene 2e showed moderate type of reactivity with 4-fluorophenylacetylene 6 and the yield of the hydroarylation product 7e was 55 % (Entry 5).

Finally, the reaction of internal alkyne diphenylacetylene 8 and 1-methyl-2-phenylacetylene 9 were examined with various electron rich arenes 2 under the above reaction conditions (Scheme 4). The results of the reactions are shown in Table 4. The reaction of diphenylacetylene 8 with

Table 3. Hydroarylation reaction of 4-fluorophenylacetylene 6 with different arenes 2 in the presence of $FeCl_3$/ AgOTf catalyst system[a].

Entry	Arene 2	Time (h)	Product 7	Yield (%)[b]
1	2a	30	7a	70
2	2b	24	7b	66
3	2c	60	7c	60
4	2d	24	7d	71
5	2e	24	7e	55

[a]Reaction conditions: Arene 2 (5.0 mmol), alkyne 6 (1.0 mmol), $FeCl_3$ (.0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 ml), CH_2Cl_2 (3.0 ml), molecular sieve 4A(3–4 pieces, 0.20~0.25g) at 30ºC.
[b]Isolated yield based on 4-fluorophenylacetylene 6.



8. R = Ph
9. R = CH_3

10. R = Ph
11. R = CH_3

Scheme 4. Hydroarylation reaction of internal alkynes 8 and 9 with different electron rich arenes 2 in the presence of $FeCl_3$/AgOTf catalyst system.

pentamethylbenzene 2a gave the hydroarylation product 10a in moderate yield (Entry 1). On the other hand, the reaction of 1-methyl-2-phenylacetylene 9 with pentamethylbenzene 2a, 1,2,4,5-tetramethylbenzene 2b, 1-bromo-2,4,6-trimethylbenzene 2c, 1,3,5-trimethylbenzene 2d, and 1,4-dimethylbenzene 2e afforded 1-aryl-1-phenylethenes 11 in moderate to good yields (Entries 2-6).

Possible Mechanism of the $FeCl_3$/AgOTf Catalyzed Hydroarylation Reaction [30]

The hydroarylation reaction between arenes and arylsubstituted alkynes in the presence of $FeCl_3$/AgOTf catalyst system is considered to be a Friedel-Crafts type reaction (Scheme 5). First of all, $FeCl_3$ reacts with AgOTf and forms a more cationic species $Fe(OTf)_3$. The resulting cationic $Fe(OTf)_3$ species attacks to the aryl-substituted alkynes and forms a more stable alkenyl cation I. The alkenyl cation I then undergoe electrophilic aromatic substitution reaction with arenes and forms the intermediate II in excellent regioselectivity. Finally, the intermediate II undergoes protonation and isomerization to form the desired 1,1-diarylalkene and completes the catalyst cycle.

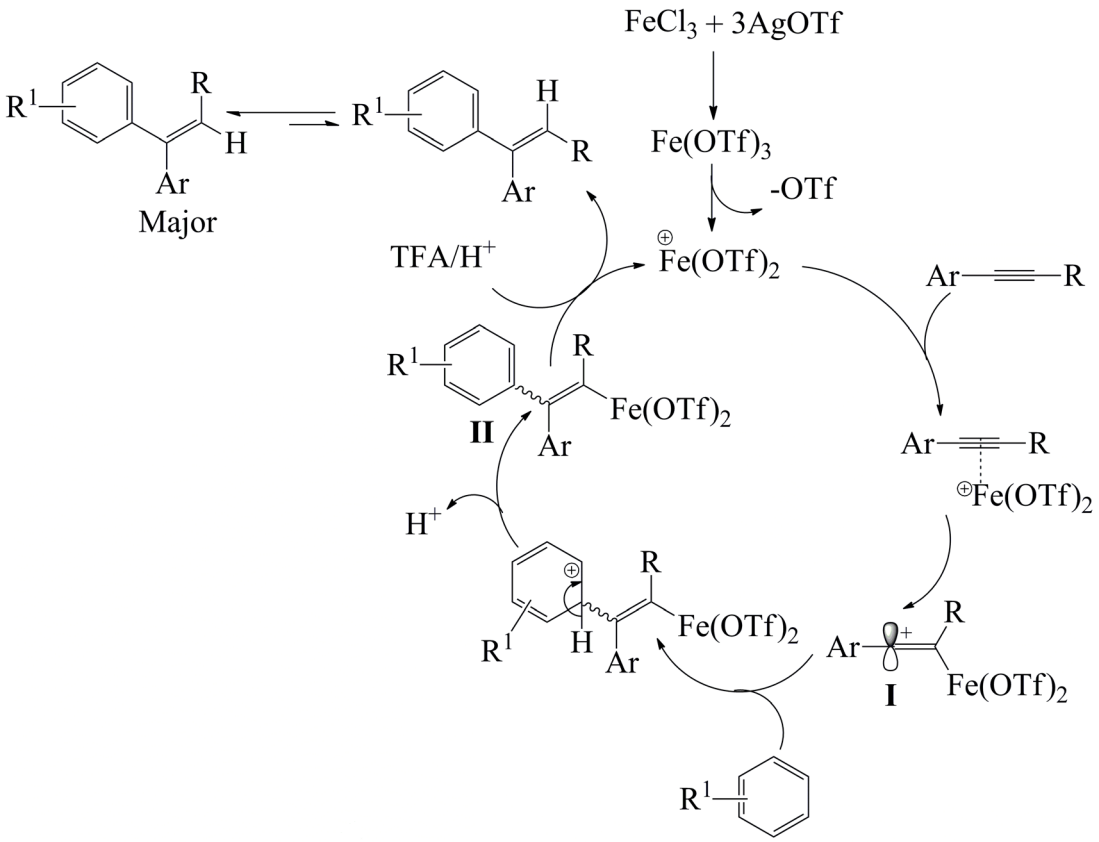
CONCLUSION

In conclusion, we have demonstrated that the $FeCl_3$/AgOTf catalyzed hydroarylation reaction of alkynes proceeds smoothly and efficiently in the presence of trifluoroacetic acid (TFA) when aryl-substituted alkynes and electron rich arenes are used. This procedure is practical as a synthetic tool of arylalkenes because of the simplicity and the mildness.

Table 4. Hydroarylation reaction of internal alkynes 8 and 9 with various electron rich arenes 2 in the presence of $FeCl_3$/AgOTf catalyst system[a].

Entry	Arene 2	Alkyne	Time(h)	Product	Yield (%)[b]
1	2a	8	48	10a	54
2	2a	9	48	11a	67
3	2b	9	36	11b	62
4	2c	9	60	11c	49
5	2d	9	36	11d	66
6	2e	9	36	11e	62

[a]Reaction conditions: Arene 2 (5.0 mmol), alkynes 8 and 9 (1.0 mmol), $FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 mL), CH_2Cl_2 (3.0 mL), molecular sieve 4A(3–4 pieces, 0.20~0.25g) at 30ºC.
[b]Isolated yield based on alkynes 8 and 9.



Scheme 5. Mechanism of the FeCl3/AgOTf catalyzed hydroarylation reaction of alkynes.

1, 1-Diphenylethene 3[11]
Yield: 0.0358g (18%); colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.30(m, 10H, Ar-H), 5.46(s, 2H, vinyl-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.08, 141.50, 128.26, 128.15, 127.69, 114.24.

1-(4-Methylphenyl)-1-(pentamethylphenyl) ethene 5a [11]
Yield: 0.2206 g (78%); white crystalline solid, Mp 85.7-86.3ºC.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20(d, 2H, Ar-H, *J* = 8.4Hz), 7.08(d, 2H, Ar-H, *J* = 7.8 Hz), 5.92(d, 1H, vinyl-H, *J* = 1.5Hz), 5.00(d, 1H, vinyl-H, *J* = 1.5 Hz), 2.32(s, 3H, Me), 2.28(s, 3H, Me), 2.23(s, 6H, 2×Me), 2.09(s, 6H, 2×Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.43, 138.89, 137.22, 137.20, 133.60, 132.28, 131.55, 129.07, 125.91, 113.31, 21.10, 17.83, 16.75, 16.54.

1-(4-Methylphenyl)-1-(2, 3, 5, 6-tetramethyl-phenyl)ethene 5b [11]
Yield: 0.2198 g (84%); white crystalline solid, Mp 115.0-116.8ºC.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18(d, 2H, Ar-H, *J* = 8.4 Hz), 7.09(d, 2H, Ar-H, *J* = 8.4 Hz), 6.96(s, 1H, Ar-H), 5.93(d, 1H, vinyl-H, *J* = 1.2 Hz), 5.00(d, 1H, vinyl-H, *J* = 1.2 Hz), 2.32(s, 3H, Me) , 2.24(s, 6H, 2xMe), 2.03(s, 6H, 2×Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.80, 141.24, 137.30, 136.93, 133.47, 131.96, 130.18, 129.09, 125.84, 113.21, 21.11, 20.13, 16.62.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(4-methylphenyl)ethene 5c [11]
Yield: 0.2143g (63%); colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16(d, 2H, Ar-H, *J* = 8.4 Hz), 7.09(d, 2H, Ar-H, *J* = 7.8 Hz), 6.99(s, 1H, Ar-H), 5.93(d, 1H, vinyl-H, *J* = 0.9 Hz), 5.00(d, 1H, vinyl-H, *J* = 0.9 Hz), 2.42(s, 3H, Me), 2.32(s, 3H, Me), 2.26(s, 3H,Me), 2.06(s, 3H, Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.87, 140.16, 137.63, 136.70, 136.13(another peak overlapped), 134.89, 129.57, 129.22, 125.71, 125.42, 113.81, 23.93, 21.39, 21.11, 19.88.

1-(4-Methylphenyl)-1-(2,4,6-trimethylphenyl) ethene 5d[11]
Yield: 0.1946g (81%); colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18(d, 2H, Ar-H, *J* = 8.1 Hz), 7.07(d, 2H, Ar-H, *J* = 8.1Hz), 6.90(s, 2H, Ar-H), 5.91(d, 1H, vinyl-H, *J* = 1.2 Hz), 5.03(d, 1H, vinyl-H, *J* = 1.5 Hz), 2.31(s, 6H, 2×Me), 2.10(s, 6H, 2xMe).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.68, 138.35, 137.32, 136.71, 136.29, 136.09, 129.11, 128.05, 125.72, 113.50, 21.09, 21.02, 20.03.

1-(2,5-Dimethylphenyl)-1-(4-methylphenyl) ethene 5e [11]
Yield: 0.0214g (9%); colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17-7.02(m, 7H, Ar-H), 5.71(d, 1H, vinyl-H, *J* = 0.9 Hz), 5.12(d, 1H, vinyl-H, *J* = 0.9 Hz), 2.33(s, 6H, 2×Me), 2.01(s, 3H, Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.32, 141.64, 137.82, 137.30, 134.98, 132.93, 130.61, 129.89, 128.99, 128.07, 126.38, 113.72, 21.11, 20.90, 19.56.

1-(4-Fluorophenyl)-1-(pentamethylphenyl) ethene 7a[11]
Yield: 0.2012g (70%); white crystalline solid, Mp 77.0-77.9ºC.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27[dd, 2H, Ar-H, *J* = 7.5(F-H) and 6.9Hz], 6.97[dd, 2H, Ar-H, *J* = 8.7(F-H) and 8.7Hz], 5.89(s, 1H, vinyl-H), 5.03(s, 1H, vinyl-H), 2.28(s, 3H, Me), 2.23(s, 6H, 2xMe), 2.09(s, 6H, 2×Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ =162.34(d, $^1J_{C\text{-}F}$ = 244.8 Hz), 147.58, 138.46, 136.13(d, $^4J_{C\text{-}F}$ = 3.68 Hz), 133.87, 132.44, 131.44, 127.64(d, $^3J_{C\text{-}F}$ = 7.43Hz), 115.16(d, $^2J_{C\text{-}F}$ = 21.0Hz), 113.98, 17.78, 16.76, 16.56.

1-(4-Fluorophenyl)-1-(2,3,5,6-tetramethylphenyl)ethene 7b
Yield: 0.1819g (66%); white crystalline solid, Mp 70.1-72.6ºC.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.21(m, 2H, Ar-H), 6.97-6.92(m, 3H, Ar-H), 5.90(d, 1H, vinyl-H, *J* = 1.2 Hz), 5.03(s, 1H, vinyl-H), 2.24(s, 6H, 2xMe), 2.03(s, 6H, 2×Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.37(d, $^1J_{C\text{-}F}$ = 244.8 Hz), 146.98, 140.82, 135.87(d, $^4J_{C\text{-}F}$ = 3.08 Hz), 133.64, 131.85, 130.41, 127.57(d, $^3J_{C\text{-}F}$ = 8.03Hz), 115.19(d, $^2J_{C\text{-}F}$ = 21.68Hz), 113.87, 20.12, 16.58.
Anal. Calcd. for $C_{18}H_{19}F$: C, 85.00; H: 7.53. found: C, 84.99; H:7.49.

1-(3-Bromo-2,4,6-trimethylphenyl)-1-(4-fluorophenyl)ethene 7c

Yield: 0.1918 g (60%); colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.19(m, 2H, Ar-H), 7.00-6.93(m, 3H, Ar-H), 5.90(d, 1H, vinyl-H, J = 0.60 Hz), 5.04(s, 1H, vinyl-H), 2.42(s, 3H, Me), 2.26(s, 3H, Me), 2.06(s, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.50(d, $^1J_{C\text{-}F}$ =245.4 Hz), 146.00, 139.69, 137.00, 136.04, 135.10(d, $^4J_{C\text{-}F}$ =3.68 Hz), 134.80, 129.68, 127.47(d, $^3J_{C\text{-}F}$ = 8.03Hz), 125.51, 115.37(d, $^2J_{C\text{-}F}$ =21.00Hz), 114.53, 23.94, 21.35, 19.84.

Anal. Calcd. for $C_{17}H_{16}BrF$: C, 63.96; H, 5.05 . found: C, 63.84 ; H: 5.08.

1-(4-Fluorophenyl)-1-(2,4,6-trimethylphenyl) ethene 7d

Yield: 0.1822 g (71%); colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.21(m, 2H, Ar-H), 6.97-6.91(m, 3H, Ar-H), 5.88(d, 1H, vinyl-H, J = 0.90 Hz), 5.07(s, 1H, vinyl-H, J = 1.2 Hz), 2.31(s, 3H, Me), 2.10(s, 6H, 2×Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ =162.44(d, $^1J_{C\text{-}F}$ = 247.2 Hz), 145.90, 137.96, 136.57, 135.99, 135.70, 128.22, 127.46(d, $^3J_{C\text{-}F}$ = 6.83 Hz), 115.24(d, $^2J_{C\text{-}F}$ = 21.00Hz), 114.19, 21.01, 20.00.

Anal. Calcd. for $C_{17}H_{17}F$: C, 84.96 ; H, 7.13. found: C, 84.94; H:7.18.

1-(2,5-Dimethylphenyl)-1-(4-fluorophenyl) ethene 7e

Yield: 0.1298 g (55%); colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.21(m, 2H, Ar-H), 7.07-6.93(m, 5H, Ar-H), 5.68(d, 1H, vinyl-H, J = 1.2 Hz), 5.15(s, 1H, vinyl-H, J = 0.9 Hz), 2.33(s, 3H, Me), 1.99(s, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.38(d, $^1J_{C\text{-}F}$ = 245.4 Hz), 148.59, 141.24, 136.83(d, $^4J_{C\text{-}F}$ = 2.46 Hz), 135.15, 132.82, 130.57, 130.06, 128.25(d, $^3J_{C\text{-}F}$ =10.5Hz), 128.07, 115.12(d, $^2J_{C\text{-}F}$ = 21.68Hz), 114.37, 20.88, 19.53.

Anal. Calcd. for $C_{16}H_{15}F$: C, 84.92 ; H: 6.68. found: C: 84.92; H: 6.77.

(Z)-1-(Pentamethylphenyl)-1,2-diphenylethene 10a[11]

Yield: 0.1763 g (54%); white crystalline solid, Mp 111.4-115.1ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-6.91(m, 11H, Ar-H and vinyl-H), 2.31(s, 3H, Me), 2.21(s, 6H, 2×Me), 2.01(s, 6H, 2xMe).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.20, 141.71, 137.64, 136.27, 133.91, 132.73, 131.16, 128.61, 128.36, 128.14, 127.83, 127.09, 126.72, 126.19, 17.19, 16.87, 16.63.

(*Z*)-1-(Pentamethylphenyl)-1-phenyl-2-methylethene 11a [14]

Yield: 0.1787 g (67%); white crystalline solid, Mp 98.0-100.0ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.15(m, 5H, Ar-H), 6.40-6.33(q, 1H, vinyl-H), 2.28(s, 3H, Me), 2.23(s, 6H, 2×Me), 2.04(s, 6H, 2xMe), 1.50-1.48(d, 3H, Me).

^{13}C NMR (75 MHz, CDCl3): δ = 141.80, 141.20, 135.97, 133.32, 132.19, 131.53, 128.22, 126.42, 125.73, 123.24, 17.15, 16.75, 16.62, 15.12.

(*Z*)-1-(2,3, 5, 6-tetramethylphenyl)-1-phenyl-2-methylethene 11b

Yield: 0.1625 g (62%); white crystalline solid, Mp 77.8-79.0ºC.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.15(m, 5H, Ar-H), 6.95(s, 1H, Ar-H), 6.41-6.34(q, 1H, vinyl-H), 2.24(s, 6H, 2×Me), 1.98(s, 6H, 2×Me), 1.50-1.48(d, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.10, 140.84, 138.53, 133.44, 132.01, 130.16, 128.26, 126.51, 125.68, 123.19, 20.19, 16.04, 15.02.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H: 8.86. found: C, 91.10 ; H :8.82.

(*Z*)-1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenyl-2-methylethene 11c[24]

Yield: 0.1682 g (49%); colourless viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.15(m, 5H, Ar-H), 7.01(s, 1H, Ar-H), 6.41-6.34(q, 1H, vinyl-H), 2.42(s, 3H, Me), 2.22(s, 3H, Me), 2.00(s, 3H, Me), 1.53-1.51(d, 3H, Me).

$_{13}$C NMR (75 MHz, $CDCl_3$): δ = 140.10, 139.92, 137.49, 136.61, 136.23, 135.08, 129.71, 128.38, 126.80, 125.49, 123.83, 23.95, 20.76, 19.51, 14.98.

(*Z*)-1-(2,4,6-trimethylphenyl)-1-phenyl-2-methylethene 11d[24]

Yield: 0.1728 g (66%); colourless viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25-7.16(m, 5H, Ar-H), 6.91(s, 2H, Ar-H), 6.40-6.33(q, 1H, vinyl-H), 2.32(s, 3H, Me), 2.04(s, 6H, 2xMe), 1.54-1.51(d, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.46, 139.91, 136.22, 135.58, 128.30, 128.14, 126.57, 125.53(another peak overlapped), 123.28, 21.06, 19.68, 14.97.

(*Z*)-1-(2,5-Dimethylphenyl)-1-phenyl-2-methylethene 11e[34]

Yield: 0.1473 g (62%); colourless viscous liquid.
^1H NMR (300 MHz, $CDCl_3$): δ = 7.26-6.98(m, 7H, Ar-H), 6.89(s, 1H, Ar-H), 6.31-6.24(q, 1H, vinyl-H), 2.32(s, 3H, Me), 2.04(s, 3H, Me), 1.60-1.58(d, 3H, Me).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.57, 141.52, 139.09, 135.02, 133.37, 130.59, 129.88, 128.16, 127.80, 126.55, 126.08, 123.55, 20.95, 18.99, 15.39.

EXPERIMENTAL

All solvents and starting materials were used during the research works as received without further purification unless otherwise indicated. ^{1}HNMR and ^{13}CNMR were recorded on a JEOL JNM-Al-300FT-NMR (300 MHz) spectrometer in $CDCl_3$ solution (TMS as an internal standard). Melting points of the pure compounds were recorded by thin disc method on a YANACO electrothermal melting point apparatus and are uncorrected. Elemental analysis was performed by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University, Japan.

General Procedure for the hydroarylation of Alkynes

Required molar amount of $FeCl_3$ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 mL), CH_2Cl_2 (1.0 ml) and molecular sieve 4A(3–4 pieces, 0.20~0.25g) were taken in a 25.0 ml quick-fit round bottom flask and stirred for about 15 minutes at room temperature. Arene (5.0 mmol), alkyne (1.0 mmol) and CH_2Cl_2 (2.0 ml) were then added into the catalysts mixture and stirred at 30ºC until the completion of the reaction. The reaction mixture was dissolved in 20 ml of dichloromethane and passed through a short path of a silica gel (2.0 g) column to remove the insoluble catalysts. The column was washed with dichloromethane. Collected dichloromethane was washed with 5% aqueous $NaHCO_3$ solution to remove the unreacted TFA and dried over anhydrous Na_2SO_4. Finally, dichloromethane was removed under reduced pressure below 40ºC. Individual pure compounds were isolated from the reaction mixture by column chromatography using silica gel as a stationary phase.

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